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Carbon Filter Test Bed Monitoring:
Part 1. Evaluation of a SAW Chemical Sensor

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The military currently uses a large number of single-pass, fixed bed carbon filter elements in their personal and collective air purification systems. A means of measuring the residual adsorption capacity of in-service carbon filter elements is virtually non-existent. As a result, filter elements are replaced after a period of service time whether they are still functional or not. To address this deficiency a miniature surface acoustic wave (SAW) chemical sensor has been evaluated as a monitor of filter bed condition. In the initial effort reported here, a polymer-coated SAW sensor has been utilized to monitor the progression of a nerve agent stimulant, dimethyl methylphosphonate, through a filter test bed filled with carbon adsorbent. Studies were carried out with the SAW sensor embedded at the end of the filter bed to monitor the effluent gas stream, and in the middle of the filter bed. In either position the real-time frequency response of the SAW sensor was monitored as a function of time. Performance of the sensor and the breakthrough characteristics of the filter bed were studied as a function of the relative humidity of the air stream and the SAW sensor position in the test bed. With minor modifications the commercial SAW sensor was found to perform well in the filter bed environment. The polymer-coated SAW sensor was able to successfully follow the progression of DMMP vapor through a filter test bed, from low to high vapor concentrations.

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CARBON FILTER TEST BED MONITORING:

PART 1. EVALUATION OF A SAW CHEMICAL SENSOR

INTRODUCTION

The military currently uses a large number of single-pass, fixed bed carbon filter elements in their personal and collective protection air purification systems. These microporous, activated carbon filters are effective at removing toxic vapors such as chemical warfare agents from contaminated air, and other less toxic chemical species. The air-purifying beds of charcoal have a limited adsorption capacity and, therefore, a limited service life regardless of the nature of the chemical compounds adsorbed. There is a strong need to be able to determine the residual life of a carbon filter after storage or use. Presently, filter elements are replaced after a preset service lifetime regardless of their condition. This method is inefficient and not cost effective, and may lead to early replacement and late replacement of exhausted filters.

Various methods have been tried to evaluate a carbon filter's residual life[1,2,3,4]. These methods include those based on colorimetric detection of particular chemical species, observation of the adsorption characteristics of an indicator chemical, measurement of a carbon's moisture content, and application of complex predictive equations. The most promising methods involve analysis of a gas sensor response from either an in-bed sample of the gas stream or from a sensor placed in a carbon filter bed's effluent gas stream. The latter has the advantage of providing a real-time measurement of the effluent condition of the filter bed, but detection of a highly toxic substance at this point does not provide advance warning of the need to replace the filter element. To address the need for an in-filter bed residual life monitor, experiments were carried out to investigate whether a miniature surface acoustic wave (SAW) gas sensor could be adapted for operation in an activated carbon filter bed.

Numerous applications of SAW chemical microsensors have been investigated since Wohltjen first reported[5] this method of chemical detection in 1979. In general, SAW sensors are very attractive environmental monitors because of their small size, ruggedness, high sensitivity, and large operational concentration dynamic range. When exposed to vapors, the SAW responds to changes in mass and modulus at its surface with a shift in frequency. Thin chemoselective polymer films are typically used as coatings on the sensors to reversibly sorb and concentrate chemical species at the sensor's surface. The nature of the interaction between the coating and the vapor molecules determines the selectivity and sensitivity of the sensor, and its reversibility[6].

The objectives of this work were to 1) design and construct a lab-scale carbon test bed to mimic conditions used in U.S. Navy shipboard filters, 2) modify existing 250 MHz SAW sensors so that they could operate successfully in the carbon test bed, 3) evaluate the performance of the SAW vapor sensor positioned at the end of the filter bed and in direct contact with the carbon adsorbent, and 4) evaluate the performance of the SAW vapor sensor and filter bed, when the sensor was positioned in the center of the carbon adsorbent.

EXPERIMENTAL

Figure 1 is a schematic of the apparatus used for the filter bed breakthrough experiments at The Naval Research Laboratory (NRL). The pneumatic section consists of a cylindrical glass tube that contains the carbon adsorbent and the SAW sensor, and a glass sparger system used to produce a vapor stream with a high flow rate and high concentration of a selected vapor at a controlled temperature. Connections throughout the apparatus were made with 3/8" stainless steel tubing, and stainless steel

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valves and fittings. Air from the house air supply, used as the carrier gas, was controlled with a Miller Nelson HCS-410 Flow, Temperature and Humidity Control System to achieve the desired linear flow velocity and relative humidity. The humidified air can be directed either through the sparger vapor generator system and the carbon test bed or directly through the test bed via a bypass valve. It can also be vented to the atmosphere. Periodically, the flow rate and the relative humidity of the flowing air stream were checked at the system vent. Air flow was referenced against a BIOS International, DryCal DC-2M, Primary Air Flow Meter. Relative humidity was periodically measured with a Testo 610 humidity/temperature measuring instrument calibrated against several saturated aqueous salt solutions.

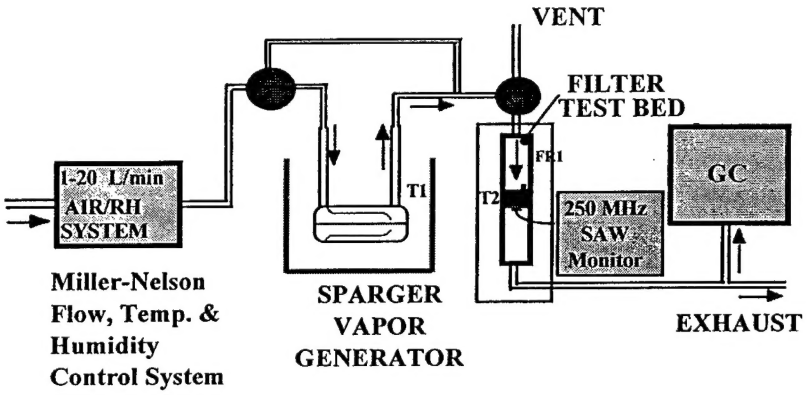

Fig. 1 – A schematic showing the carbon test bed and vapor generation system

The unimpregnated activated carbon adsorbent used in these studies was 12x30 mesh BPL lot #0325G (Calgon Carbon Corp.). Carbon for each experiment was dried for at least two days at 110°C in vacuum. The carbon was then either tested dry or preconditioned before use at the same relative humidity at which it was to be subsequently tested. Preconditioning was accomplished by allowing equilibration of the carbon with the water vapor in the air above a saturated aqueous salt solution known to maintain a constant humidity at a given temperature. Fifteen gram samples of dry or preconditioned carbon were used in each breakthrough experiment. The weighed carbon sample was poured into a 3 cm i.d. glass tube to give a bed depth of approximately 5 cm. The carbon was retained at the gas inlet by a sintered glass disk.

Dimethyl methylphosphonate (DMMP) (97%, Aldrich Chemical Co.) was used, as received, to generate the vapor challenge to the carbon filter bed in the breakthrough experiments. The DMMP sparger tubes at 25°C were gravimetrically calibrated to deliver a vapor concentration of approximately 1500 mg m^{-3}. The total flow through the carbon was 10 L min^{-1} which corresponds to a linear velocity of 24 cm s^{-1}.

A ST-cut quartz, 2-port, 250 MHz SAW resonator with an on-chip resistive temperature sensor (Microsensor Systems, Inc., MSI) was used as the sensor in the breakthrough experiments. The resonator was spray coated with 250 kHz or approximately 50 nm of fluoropolyol film (NRL material). Both the group delay and the insertion loss of the resonator were monitored during the coating process. In general, the group delay of a device was no less than 4.5 microsecond and the unmatched insertion

loss of the device was no more than 18 dB after the coating process. A loop oscillator circuit was used to interrogate the resonance frequency of the polymer-coated SAW sensor. The SAW resonator and the electronics assembly, supplied by MSI, was fitted into a 2 cm x 2 cm square printed circuit board. A thin layer of a low-loss material, polystyrene Q-Dope (GC Electronics), was used to protect the electronics, especially the amplifier, from the carbon. The operating temperature of the SAW resonator was monitored via the on chip temperature sensor with a four-wire resistance measurement technique. The SAW oscillator was powered by a 5 volt regulator.

The data acquisition system consisted of a frequency counter (Philips 6674) and a digital multimeter (Keithley 129A). Both instruments were connected via an IEEE-488 bus, and an IBM compatible personal computer was used to collect the data. A data acquisition program was developed to interrogate the instruments. The measurement gating time for the frequency counter was set to 1.0 sec which translated to a 10 Hz measurement resolution for the SAW sensor. The resistance of the temperature sensor was acquired at approximately a one second interval while the output of frequency counter was downloaded at the end of each corresponding gate time.

In most tests described in this work, the SAW sensor was positioned at the test bed exit but in direct contact with the carbon adsorbent as shown in Figure 2a. In some experiments, the sensor was located in the center of the test bed within the bulk of the adsorbent. In all cases, the sensor was positioned parallel to the test bed cross section so that its coated surface faced the incoming air flow. Real-time monitoring of the in-bed SAW sensor response was accomplished via a computer-controlled data acquisition system. The real-time sensor response was used to study the effects of relative humidity on the breakthrough time of the carbon adsorbent. It should be noted that no active temperature control of the filter bed was used in the breakthrough experiments described and its temperature drifted with the laboratory temperature.

TABLE 1 – Filter Bed Breakthrough System Parameters

Adsorbent Material	12 x 30 mesh BPL carbon
Mass of Adsorbent	15 g
SAW Operating Frequency	250 MHz
Polymer Coating	FPOL
Approx. Coating Thickness	250 kHz (50 nm)
Test Vapor	DMMP
Vapor Feed Concentration	1500 mg/m^3
Filter Bed Depth	5 cm
Filter Bed Diameter	3 cm
Linear Flow Rate	24 cm/s
Mass Transfer Zone	1.8 cm
Temperature	25-30°C
Relative Humidity of Flowing Air	0-100 %

Table 1 summarizes the filter bed breakthrough system parameters used in this work. Test parameters that were unchanged throughout the series of experiments include the test vapor, the vapor feed concentration, and the linear flow rate. Parameters that were altered include the relative humidity (33, 50 or 75%) of the flowing air stream and the initial condition of the carbon adsorbent (dry or containing preadsorbed water).

Particulate removal from the air stream was accomplished by fabricating a lid for the SAW sensor. Stainless steel lids were fabricated that had a 6 mm diameter hole above the SAW sensor. A

polycarbonate membrane filter with a porosity of 0.2 μm was press fit inside the lid and a miniature stainless steel frit (80 mesh) provided mechanical support to the membrane filter. The lid press fit over the SAW sensor and allowed air and vapor to diffuse in and out of the sensor while screening particulates. With this configuration the air stream passing through the filter bed was passively sampled by the SAW sensor. A schematic of the SAW sensor with its lid is shown in Figure 2b.

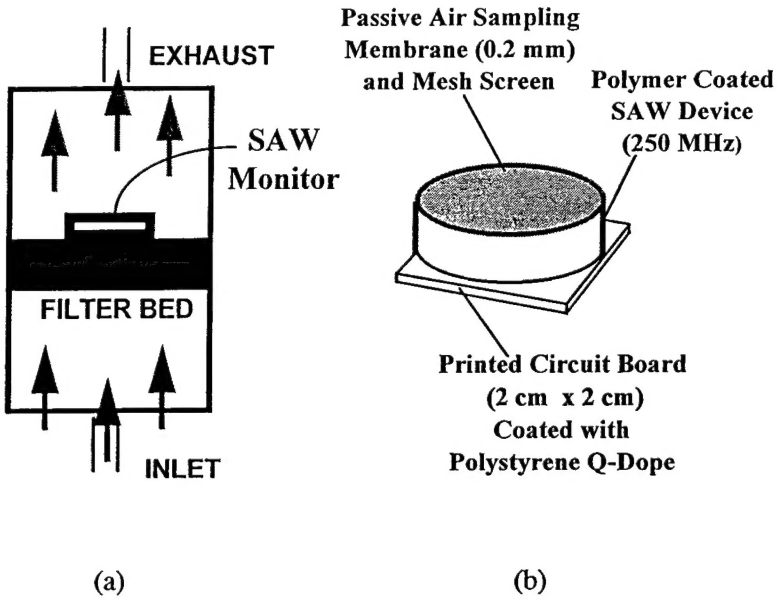

Fig. 2 – Close up view of (a) filter test bed showing the SAW sensor configured at the end of the bed in contact with the carbon adsorbent and (b) the SAW sensor with lid and a 2 cm x 2 cm printed circuit board that is coated with polystyrene Q-Dope on its back side. The lid fashioned for the SAW sensor contains a passive air sampling polycarbonate membrane filter with 0.2 μm porosity

RESULTS AND DISCUSSION

Initially Dry Carbon Beds

DMMP breakthrough of test beds initially packed with dry carbon from two separate breakthrough experiments are shown in Figure 3. The two breakthrough experiments differed by using humid air carrier gas with different relative humidities. The upper curves in the figure show the frequency response of the fluoropolyol-coated SAW sensor to a DMMP vapor feed concentration of approximately 1500 mg m^{-3}. The lower curves show the response (in ohms) of an on-chip resistor for monitoring the temperature of the SAW. In both experiments, the SAW sensors were embedded in the carbon adsorbent at the test bed exit.

Experimental results, such as those in Figure 3, indicate that vapor breakthrough of the carbon test bed is successfully monitored with the SAW sensor response throughout the entire process up to the delivery concentration of 1500 mg m^{-3}. At complete breakthrough of the DMMP challenge the frequency response of the sensor was more than 100 kHz. Smaller frequency responses early in each experiment indicate incipient bed breakthrough of lower DMMP concentrations. The results also showed that the SAW sensor performed well in the filter bed environment regardless of the high linear flow rate and high vapor concentration used, and in the presence of particulate matter.

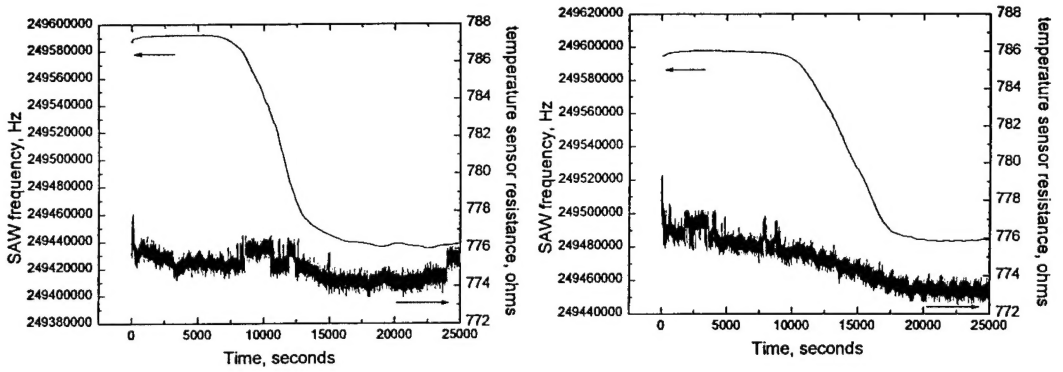

Fig. 3 – DMMP breakthrough curves on initially dry carbon with the % relative humidity of the air carrier gas varied as follows: (a) air at 50% R.H. and (b) air at 75% R.H. The SAW sensor was embedded in the carbon adsorbent at the test bed exit in these experiments. The top curves are the frequency responses of the coated SAW. The bottom curves are the resistances of the temperature sensors

The results from several breakthrough experiments on initially dry carbon with humid air carrier gas at different relative humidities are summarized in Figure 4. As seen in the figure, DMMP breakthrough times on the initially dry carbon adsorbent increase with increasing relative humidity of the carrier gas. For example, the 1% breakthrough time for DMMP on the dry carbon adsorbent occurred at approximately 6000 s, 7000 s, and 8000 s with humid air carrier gas at 33%, 50% and 75% relative humidity, respectively.

Vapor penetration of adsorbent beds is often described by the Wheeler kinetic breakthrough model[7,8,9]. This model describes breakthrough in terms of a kinetic adsorption capacity and an adsorption rate constant. Based on this model, an explanation for the breakthrough results observed in humid air is that there is an increase in adsorption capacity for highly soluble vapors (such as DMMP) on activated carbon at high water loading. Another explanation is that an increase in humidity lowers the kinetic rate constant rather than altering the adsorption capacity.

Breakthrough experiments were also carried out on initially dry carbon with the position of the SAW sensor in the adsorbent varied. In one case, an inactive sensor was placed in the center of the test bed and its effect on the vapor breakthrough was measured by a second active sensor positioned at the test bed exit. Incipient breakthrough in this experiment occurred at approximately the same time for experiments in which no sensor was present in the middle of the bed.

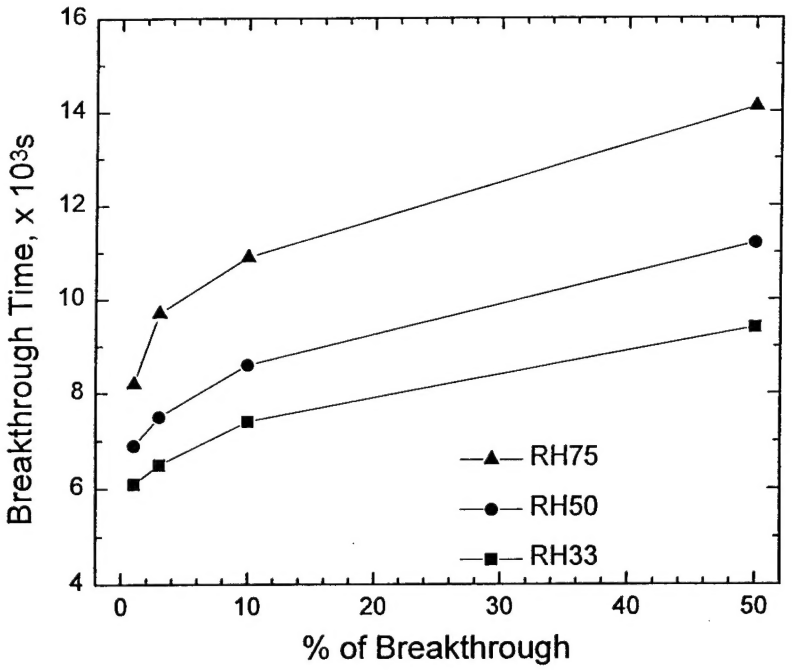

Fig. 4 – DMMP breakthrough times on initially dry carbon vs. % relative humidity of the air carrier gas. The data are taken from breakthrough curves such as those shown in Figure 3 with the SAW sensor embedded in the carbon adsorbent at the test bed exit

In another experiment, the active SAW sensor was positioned in the center of the carbon test bed. In effect this can be likened to positioning the sensor between two short beds of adsorbent and measuring breakthrough of one short bed (approximate depth 2.5 cm). As expected, the vapor breakthrough time measured through the shorter carbon bed was less than that measured through the usual longer bed (depth 5 cm). This experiment demonstrated the feasibility of incorporating a SAW sensor in the carbon adsorbent in the middle of the test bed, and the previous experiment confirmed that the positioning of a SAW sensor in the middle of the bed did not adversely effect the performance of the filter bed.

Humidity Preconditioned Carbon Beds

DMMP breakthrough experiments were also carried out on carbon test beds containing water preadsorbed at 33%, 50% and 75% relative humidity. Generally, breakthrough times on preconditioned carbon were longer than those on dry carbon. For example, a comparison of two experiments run with humid air carrier gas at 33 % relative humidity showed that the 1% breakthrough time for DMMP on dry carbon occurred at approximately 6000 s while on carbon preconditioned at 33% relative humidity it occurred at 12000 s.

SUMMARY AND CONCLUSIONS

The real-time response of a SAW sensor embedded in the carbon of a filter test bed was used to evaluate the SAW sensor as a filter bed lifetime monitor, and to monitor the effects of relative humidity on the breakthrough time of the adsorbent. The experiments performed to date yield the following conclusions regarding the performance of the SAW sensor and its effect on the filter bed performance:

1. The SAW sensor performed well in the filter bed environment whether embedded in the carbon adsorbent at the test bed exit or positioned in the center of the test bed. The sensor also operated well with a protective lid in the presence of particulate matter.

2. The SAW sensor was able to successfully monitor the entire breakthrough process, from low to high DMMP vapor concentrations. It was also able to withstand the high linear flow rate used in the breakthrough experiments.

3. The SAW sensor was able to monitor filter bed breakthrough without active temperature control of the filter bed and under different humidifying conditions.

4. The filter bed performance was not degraded when the SAW sensor was embedded in the carbon adsorbent at the exit of the filter bed nor when the SAW was positioned in the center of the test bed.

FUTURE WORK

While carrying out filter bed breakthrough experiments at high relative humidities (50 and 75%) it became apparent that the vapor generation system needed modification since water vapor from the humidified air stream collected in the DMMP sparger tubes. To overcome this problem, a second Miller Nelson Flow, Temperature and Humidity Control System has already been added to the vapor generation system described in this report. In the modified vapor generation system one Miller Nelson Control unit generates dry air which is directed through the spargers to produce an air stream with a known vapor concentration and a second control unit generates a humid air stream. The air streams are combined in a glass mixing chamber located in front of the test bed inlet. Since the flow rate of the humidified air is known, the diluted vapor concentration can be calculated.

Filter bed breakthrough experiments are continuing with the carbon test bed and modified vapor generation system described. New experiments will emphasize placement of the SAW sensor in the middle of the test bed. Other coatings for the SAW sensor and other sensor devices will be investigated.

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